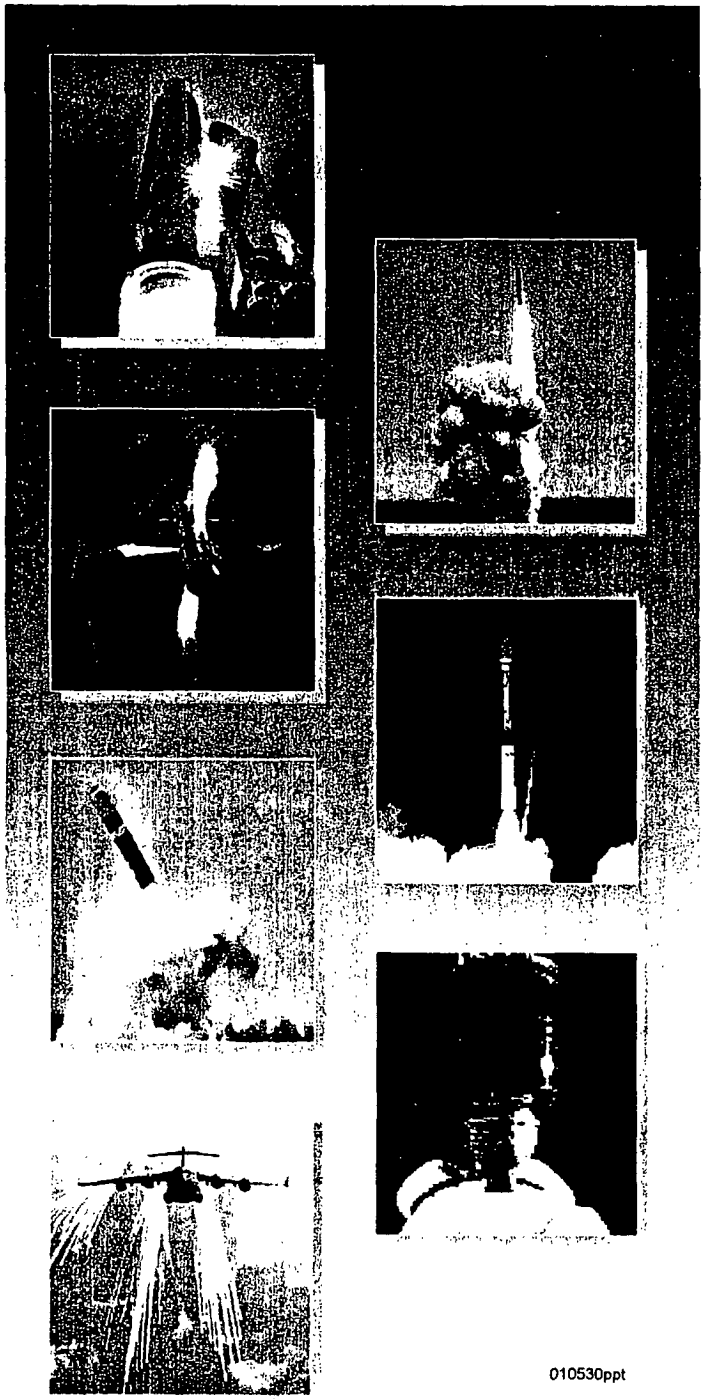

010530ppt

Chemical Fingerprinting Program for RSRM Critical Materials

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ATK
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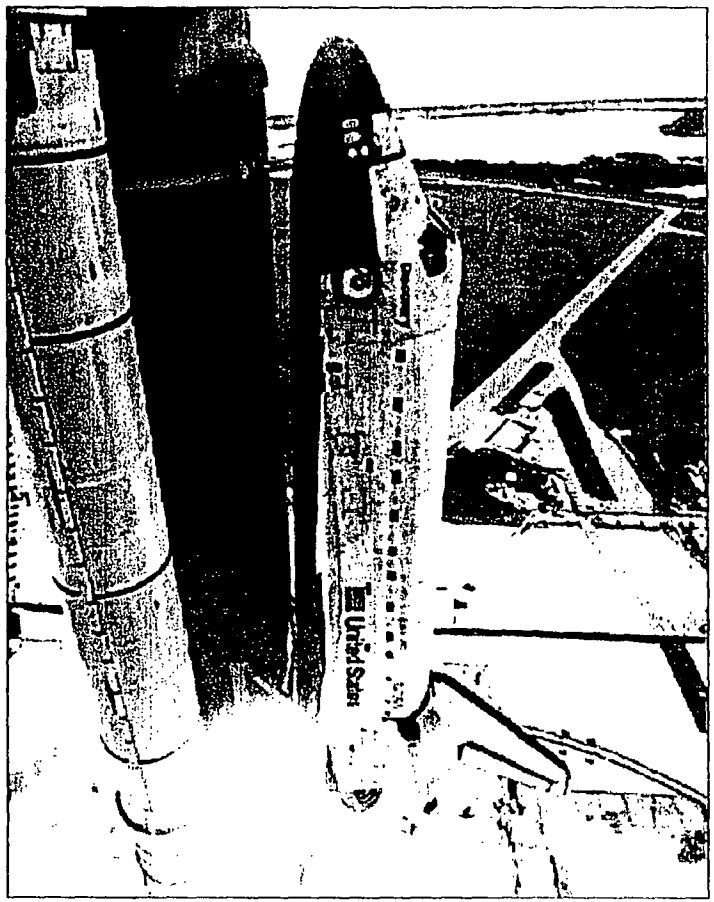
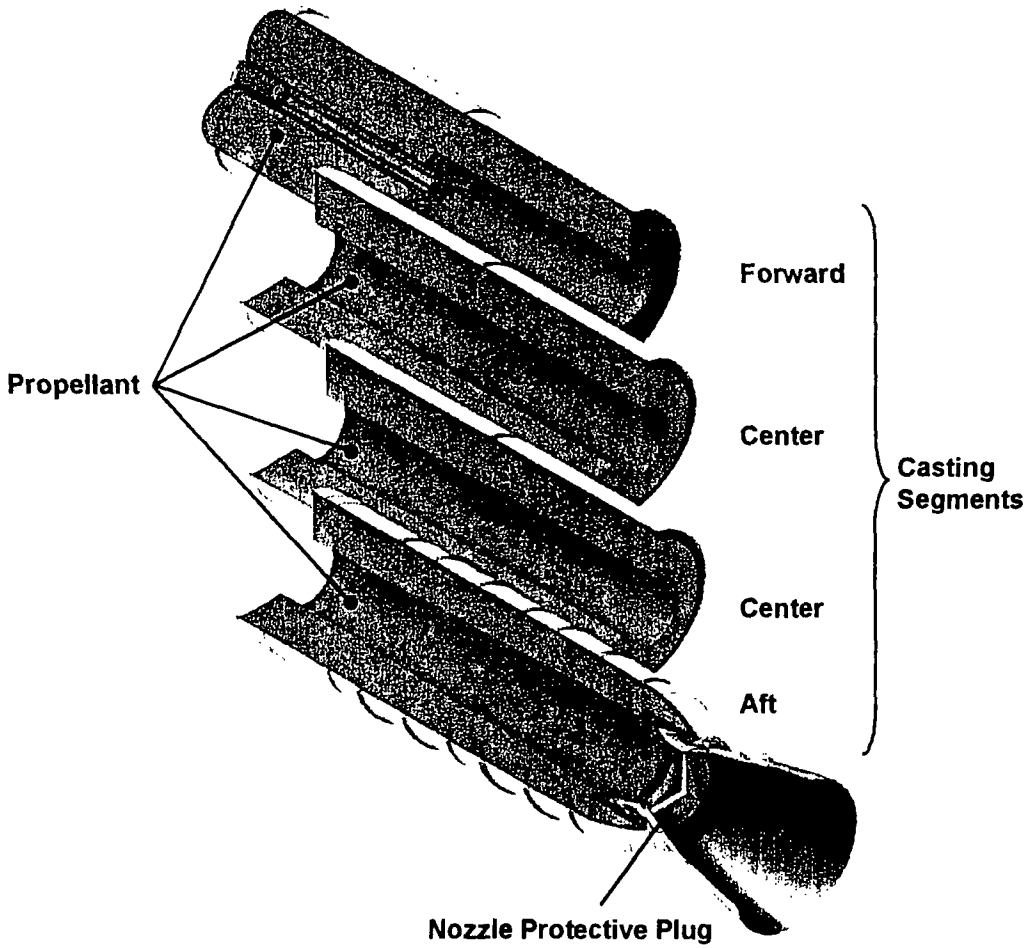
Presentation Outline



- Background
- Objectives and Approach
- Accomplishments
  - Description of Database Viewer
  - Success Stories
  - Direct and Additional Benefits
- Continuing Challenges
- Acknowledgements

Reusable Solid Rocket Motor (RSRM) Components Involving Critical Materials

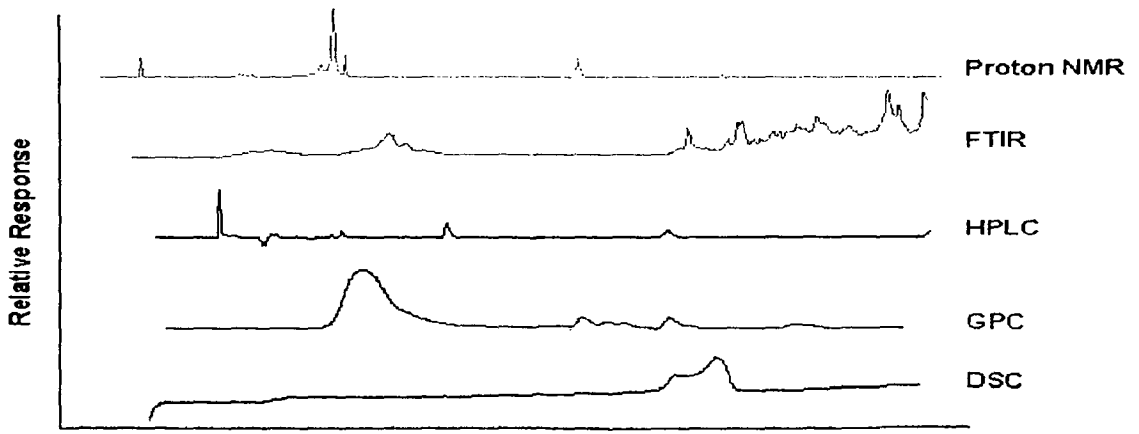


- Segmented steel case
- Movable nozzle
- Case-bonded, composite solid propellant
- Elastomeric internal insulation
- Nozzle ablative liner
- Nozzle insulator and structural shell
- Clean bonding surfaces
- Effective adhesives

Background: Chemical Fingerprint Definition

Diagnostic Combination of Analytical Methods for Detailed Characterization of a Material

- Key importance is a chemical fingerprint that can be used to identify a material, to differentiate it from similar looking materials, or lead to its source
- In the past, fingerprinting methods were used to characterize materials and processes
  - Following a failure or noncompliance
  - Ad hoc, reactive, and incomplete generation and storage of data
  - Database scattered over dozens of file cabinets
  - Few techniques were adopted for receiving inspection/process control



Objectives of Chemical Fingerprinting
(Recognize, Reduce, Resolve Problems)

- Detailed understanding of material composition
- Enhanced ability to detect changes in a material due to vendor changes or subtier supplier changes
  - Improved acceptance testing based on chemical composition
- Improved understanding of how a material works, ages, degrades, etc.
- Standardized approach to material fingerprinting
- Develop methods for monitoring all key ingredients
- Develop a comprehensive material database
- Reduced probability of unexpected and unrecognized changes to critical materials and processes

Approach: State of Art Facilities

- **Chemical Characterization**
  - **NMR (300 and 400 MHz)**
  - **Surface analysis**
    - ESCA/XPS
    - Auger
    - SIMS
    - ISS
  - **RAMAN / FTIR / NIR**
  - **Metals analysis**
    - ICP emission
    - AA/GFAA
    - ICP-MS
  - **X-Ray Fluorescence**
  - **Chromatography**
    - HPLC/HPLC-MS
    - GPC
    - GC (various detectors)
    - GC-MS
    - Ion chromatography
  - **Flow injection auto analyzer**
  - **CHN O/S**
  - **Classical techniques**
  - **Asbestos identification**
- **Thermal Analysis**
- **Mechanical Properties**
- **Non Destructive Analysis**

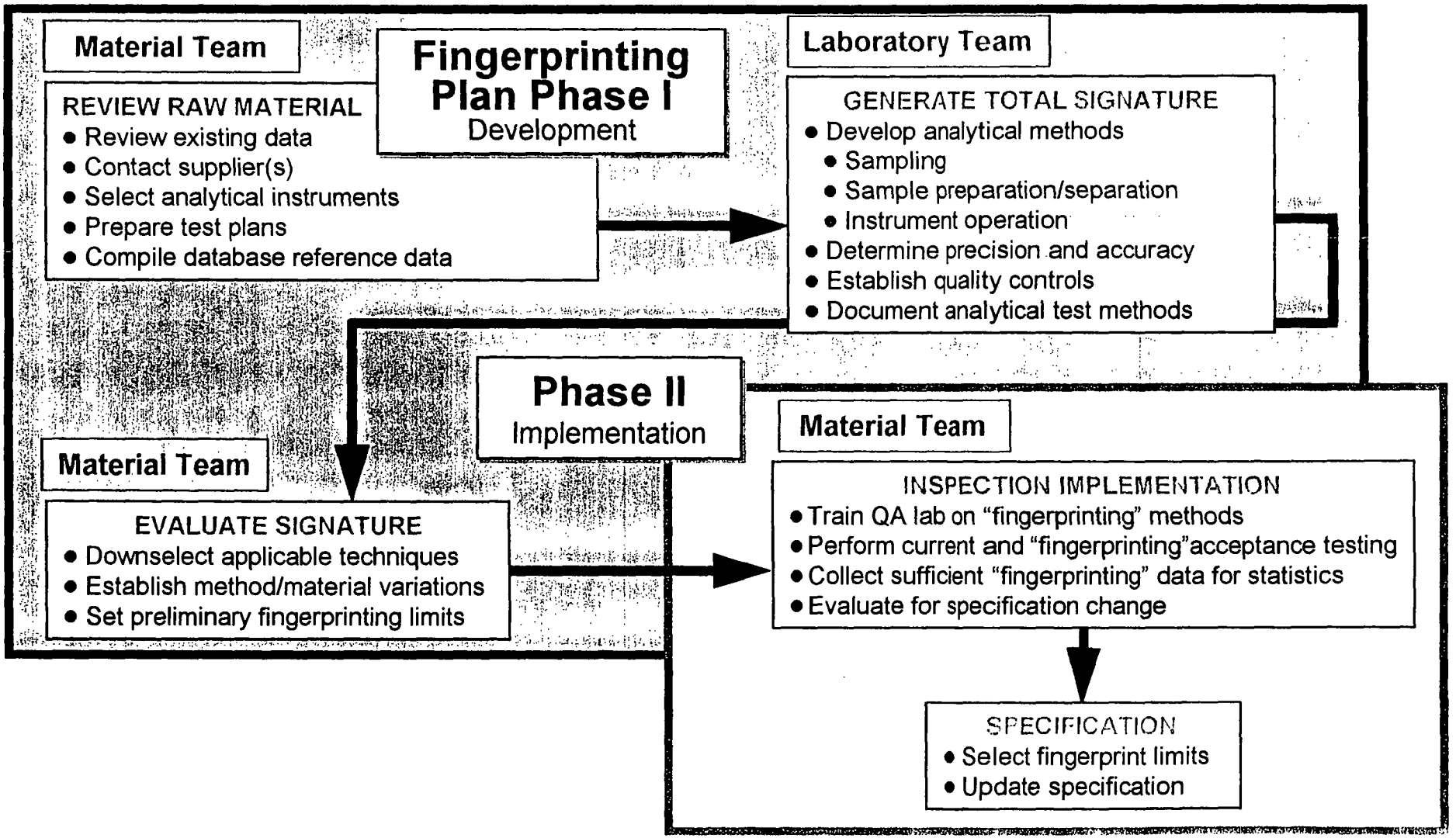
Approach: Material Team

Team Members

Material Specialist
M&P Specialist
Design Engineer
Procurement Quality Engineer
Manufacturing Engineer
Process Control Lab

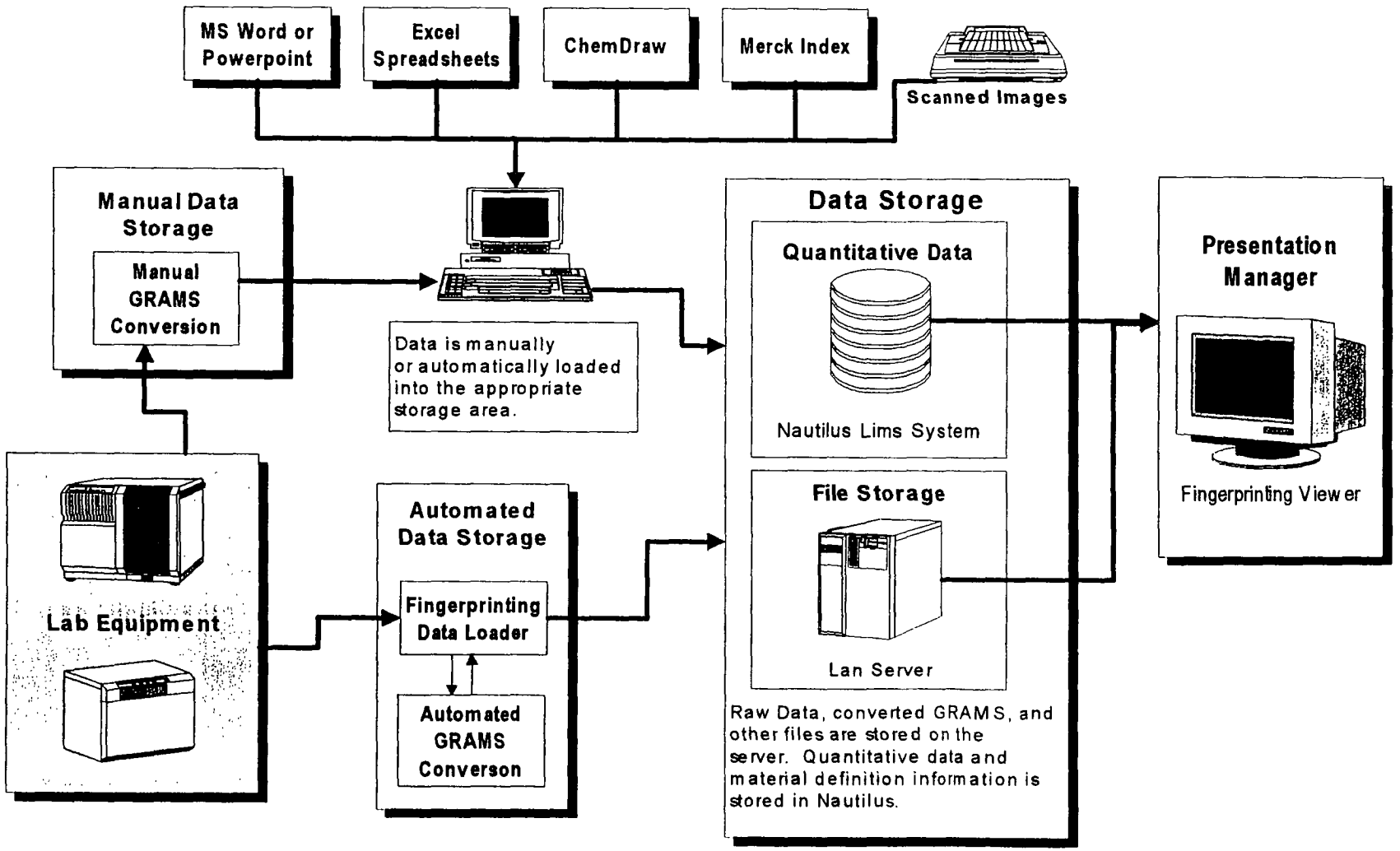
R&D Analytical Laboratories
R&D Materials and Process
S&E Engineering
Quality
Operations
Quality Lab (material receipt)

Material Fingerprinting Approach



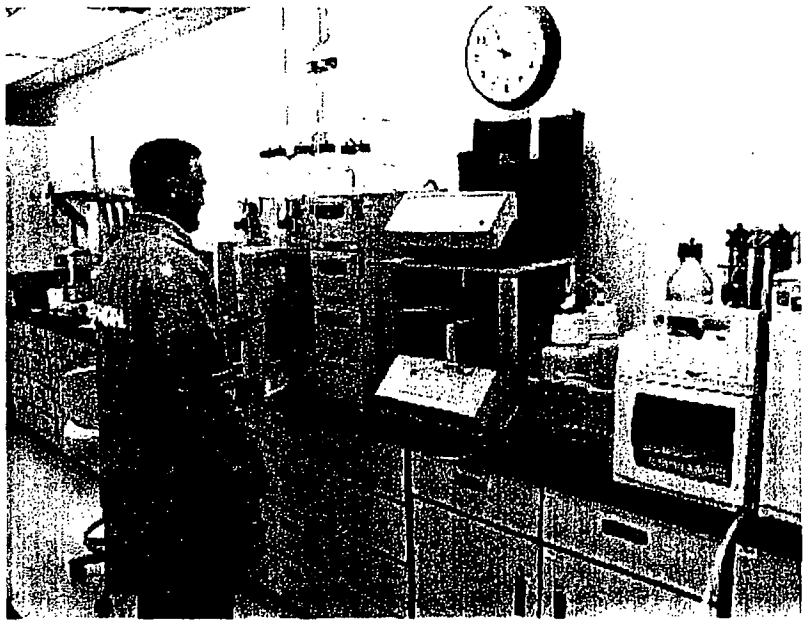
Data Management

Fingerprinting Data Manipulation and Storage



Database Components and Software
(No Commercially Available Integrated System: Integration and Data Parsing Developed Internally)

- Server-based PC Network: Novell®
- Data loader and Viewer: developed software programs internally using PowerBuilder®
- Oracle® database
- LIMS (Lab Information Management System) software: Nautilus® R2B2, LabSystems
- Spectroscopic/ Chromatographic Data Viewer: Grams/32® v. 7.0, LabSystems, Galactic Industries



Ion Chromatography Analysis

Accomplishments: RSRM Fingerprinting Materials

- 55 Materials completed or in process
  - 11 Solvents or cleaning solutions
  - Phenolic resin and 3 phenolic composites
  - 4 Compounded rubber insulations
  - 2 Propellant systems
  - 10 Polymeric components
  - 3 Sealants and ablative compounds
  - 5 Rubber adhesives
  - 3 Epoxy based adhesives
  - 5 Paints and primers
  - 7 Inorganic fillers, abrasives and reactive components
  - 1 Corrosion inhibiting grease

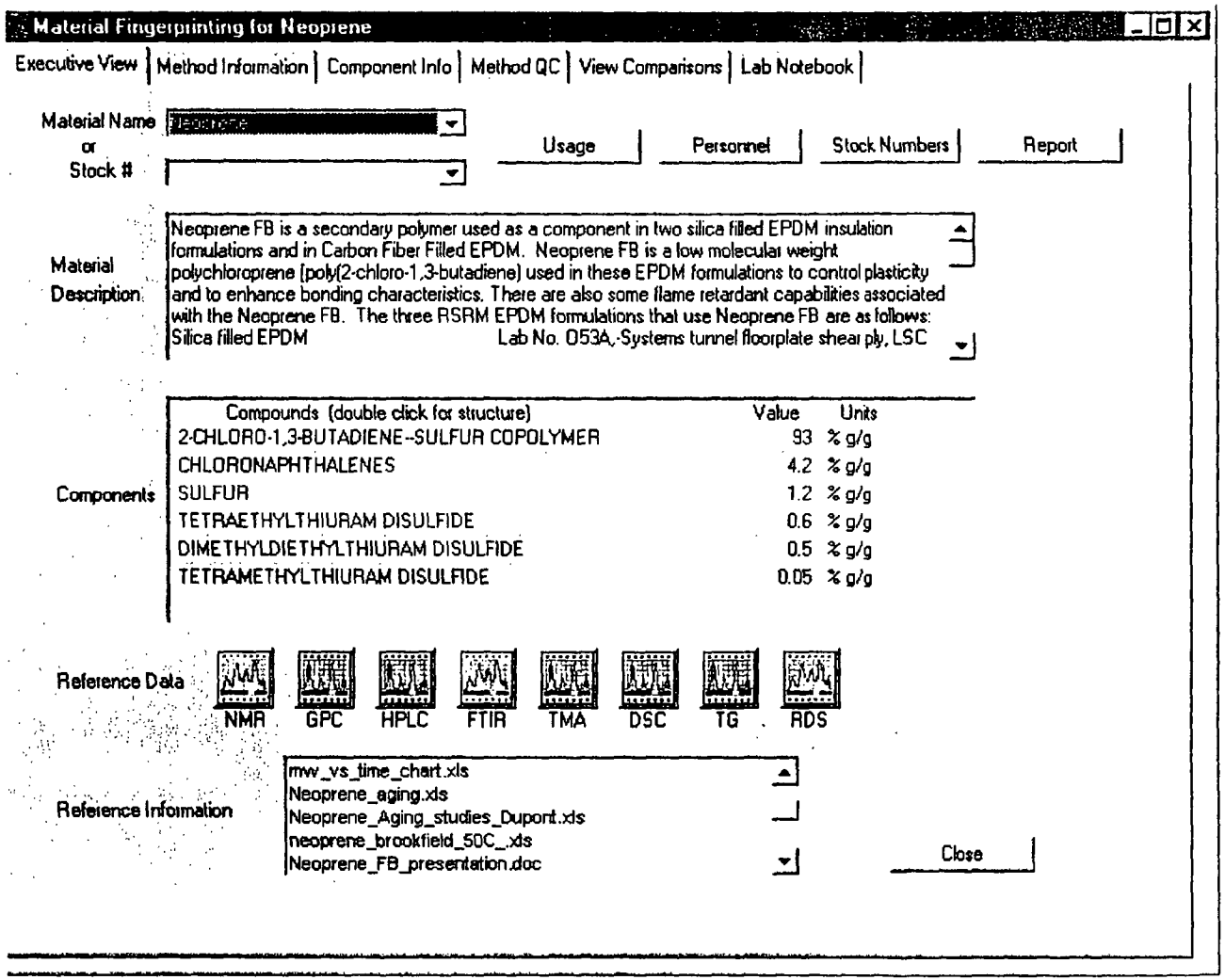
Accomplishments: Database Viewer Features

- Executive view
  - Material overview, reference documents, data examples
- Method information
  - Chemical characterization methods
- Component information
  - Trend analysis and visualization of key analytes
- Method quality control
  - Trend analysis of QC parameters
- View comparison
  - Direct graphical overlay of raw spectroscopic and chromatographic data
- Lab notes

Material Fingerprinting Success Example

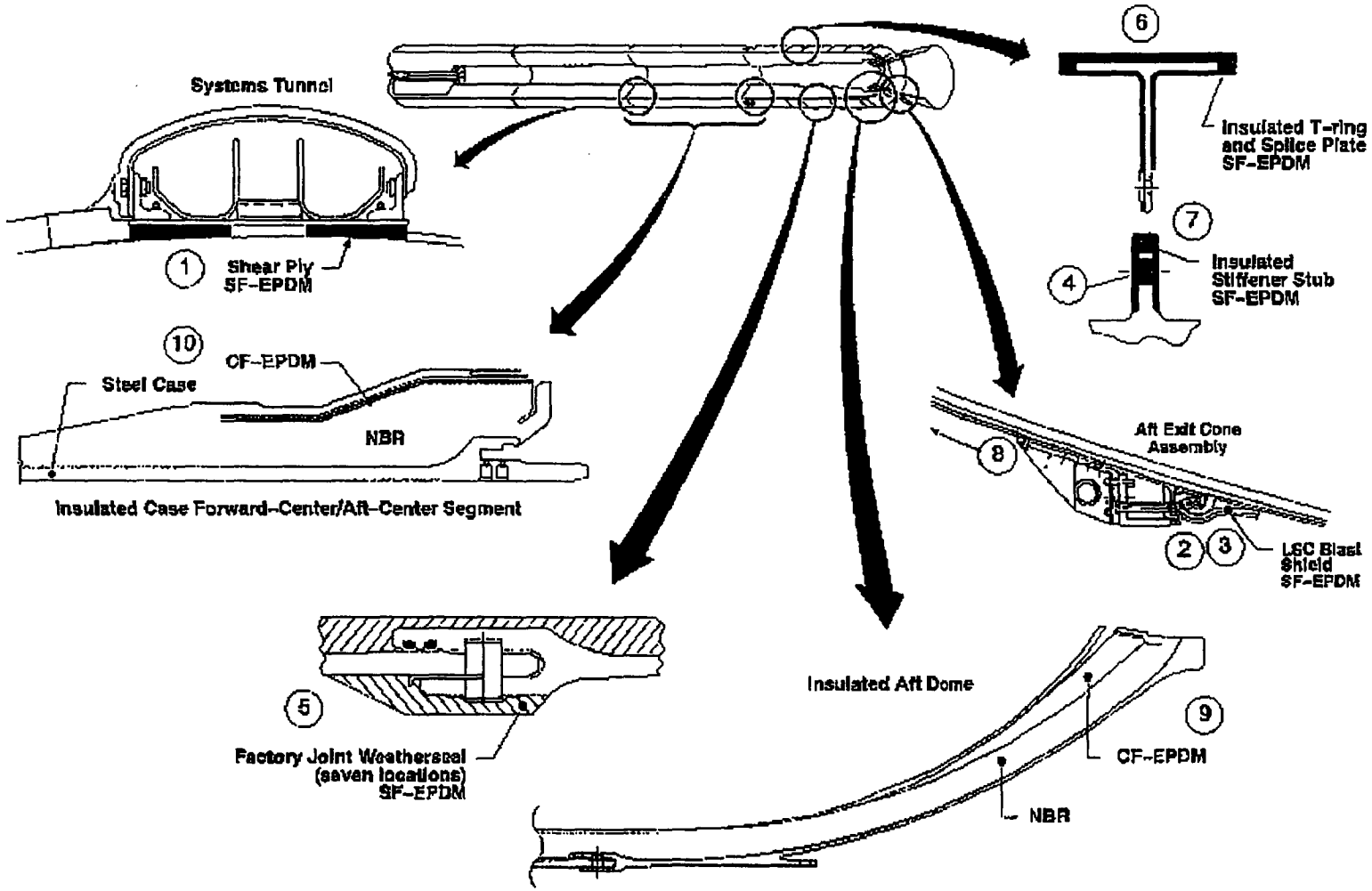
- Neoprene FB
  - Secondary polymer used as a component in case insulation EPDM formulations
  - Material no longer produced
  - Fingerprinting showed that under proper storage conditions: Neoprene FB could be stored over 10 years and still meet specification
    - Storage at 40°F, low humidity, and minimal light
    - Stockpiled 100,000 lb till new EPDM formulation can be qualified
  - Test methods developed to ensure material is well within specification
    - Viscosity measurement performed as a check at the vendor's storage site, while the GPC and FTIR analyses confirm the molecular weight distribution and the chemical composition
  - Defense program experienced solvating problem with gum stock for carbon fiber EPDM
    - Fingerprinting knowledge allowed immediate identification of the problem
    - Corrective action given on controlling Neoprene FB

Presentation Module: Executive Screen for Neoprene FB



Material Example: Neoprene FB in EPDM

EPDM Usage in Booster Motor



Method Information Screen

Material Fingerprinting for Neoprene

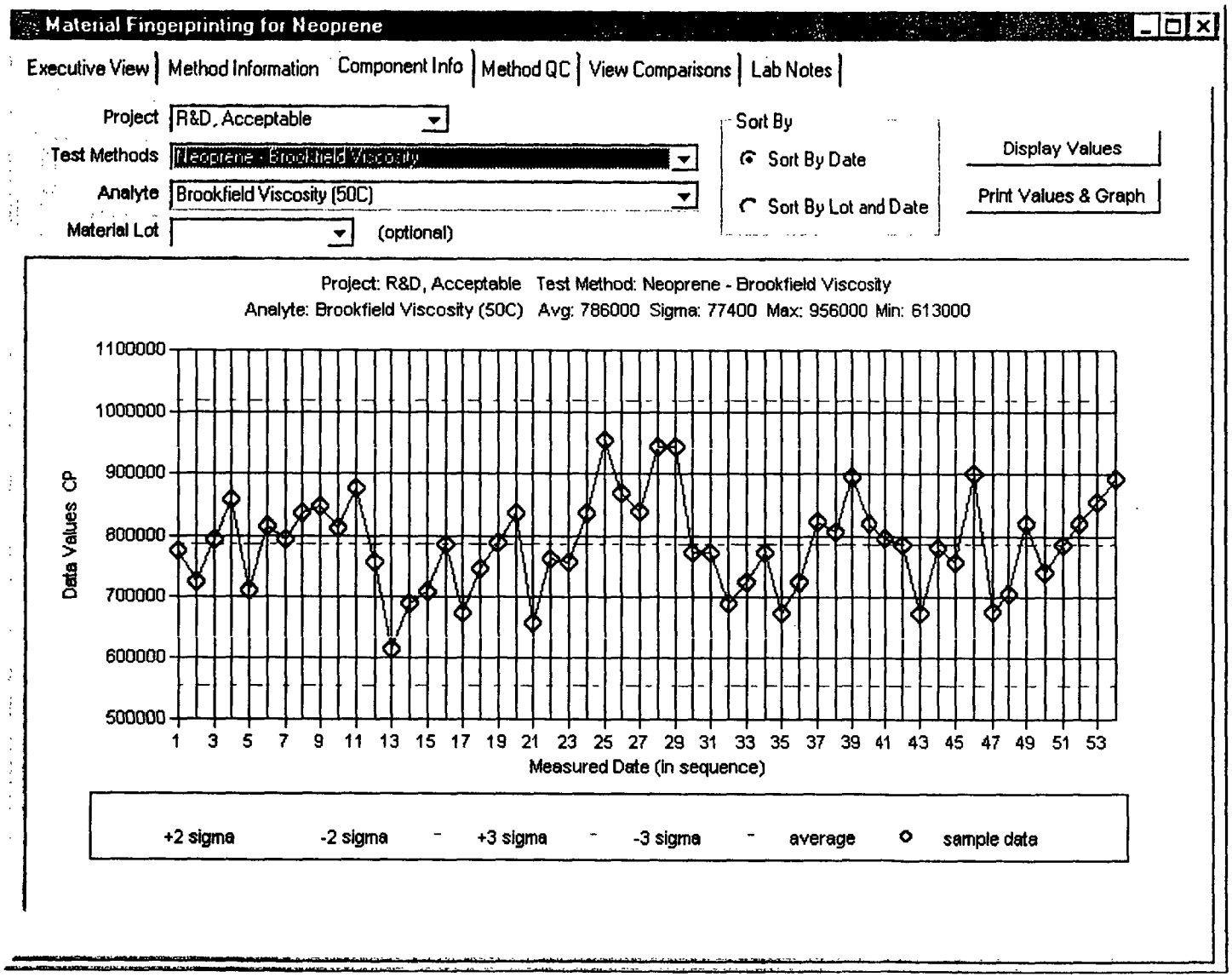
Executive View | Method Information | Component Info | Method QC | View Comparisons | Lab Notebook

Description	Method Ref.	Test	Dept. Name	Dept. Abbr.
C,H, and N Elemental Analysis	LTP-33H1-1030-FP1800	CHN_F1800	Auto Analyzer	AU
DSC Analysis - Low Temperature Scan	LTP-33H1-1176-FP1500	DSC_F1500	Differential Scannning Calorim	DSC
Neoprene FB - GPC Analysis	LTP-33H2-1099-FP0300	GPC_F0300	Gel Permeation Chromatography	GPC
FTIR Analysis	LTP-33H2-1069-FP0700	FTIR_F0700	Infrared Spectroscopy	IR
FTIR Analysis - Quality Compare	LTP-33H2-1069-FP0700	FTIR_F0700_QC	Infrared Spectroscopy	IR
Neoprene - Analysis by HPLC	LTP-33H2-1136-FP0100	LC_F0100	Liquid Chromatography	LC
Neoprene - Brookfield Viscosity	LTP-33H1-1101-FP2100	ME_F2100	Mechanical Testing	ME
Neoprene - RDS	LTP-33H3-1100-FP2000	RDS_F2000	Mechanical Testing	ME
Neoprene - ICP AES Analysis	LTP-33H1-1102-FP1001	ICP_F1001	Metals Analysis	MT
NMR Analysis (Carbon-13)	LTP-33H1-1079-FP0800	NMR_F0800_C13	Nuclear Magnetic Resonance	NMR
NMR Analysis (Proton)	LTP-33H1-1079-FP0800	NMR_F0800_H	Nuclear Magnetic Resonance	NMR
Thermal Gravimetric Analysis	LTP-33H1-1156-FP1600	TG_F1600	Thermogravametric Analysis	TG

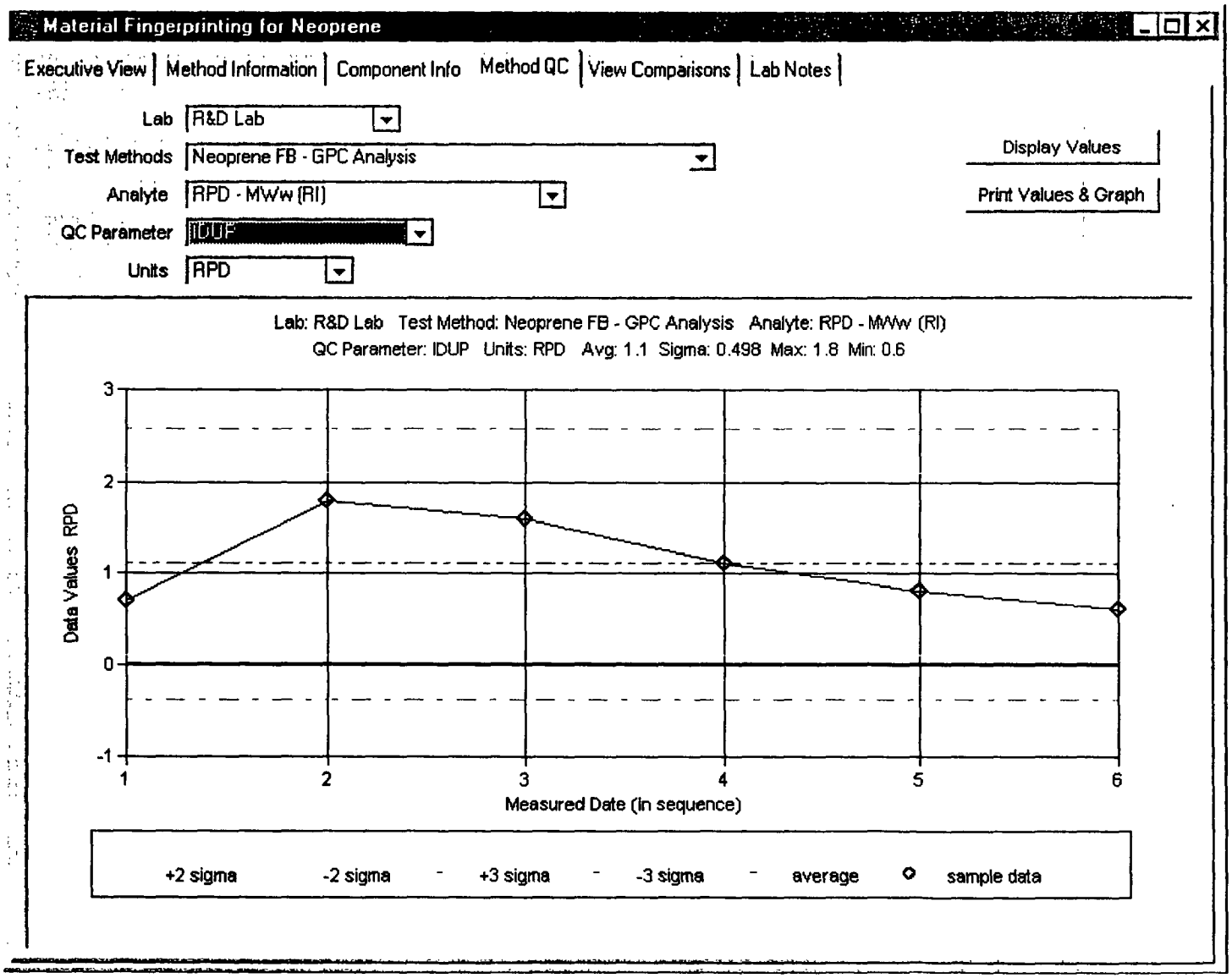
Highlighted items are primary tests

Material Account # 0378

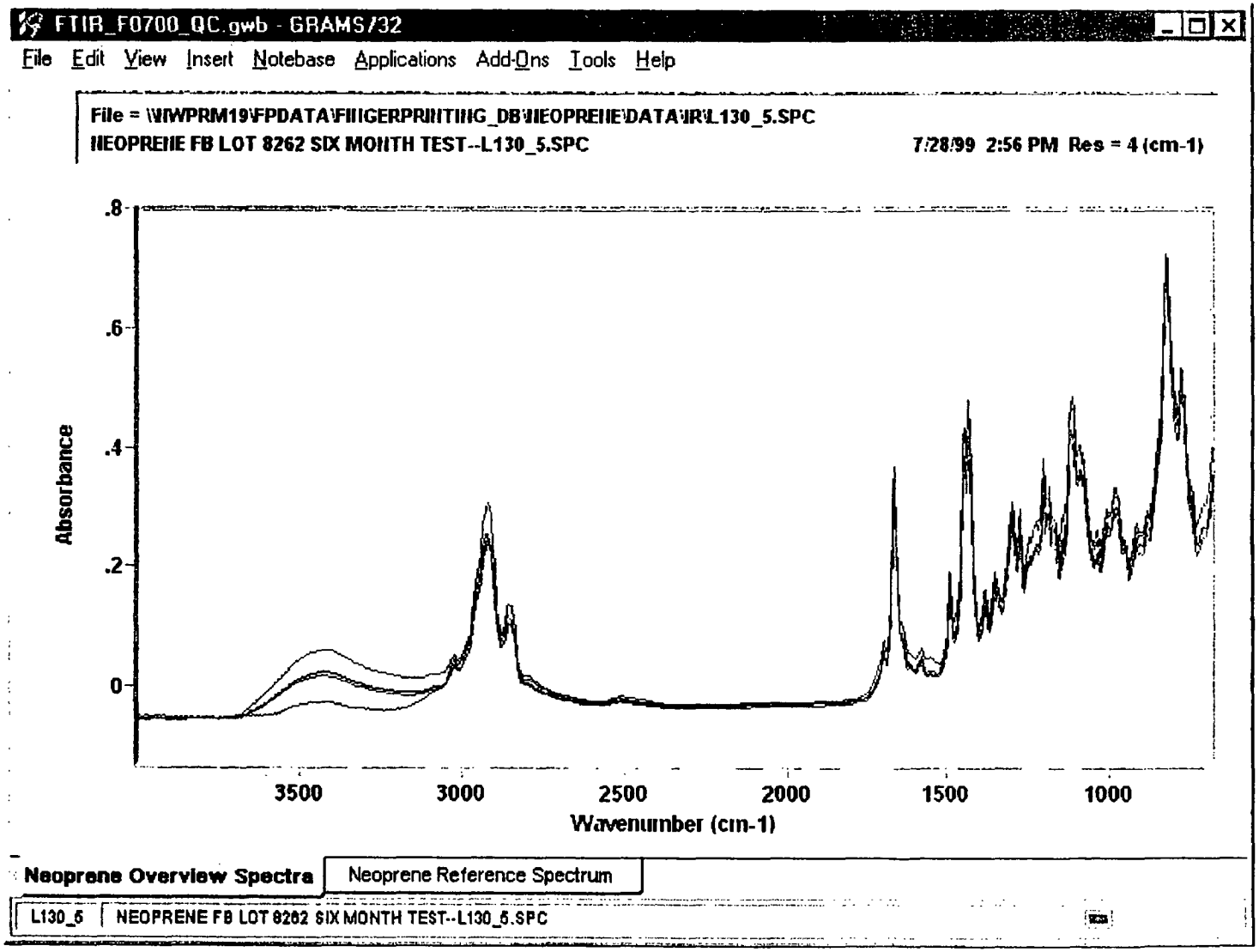
Component Info: Analyte Trends



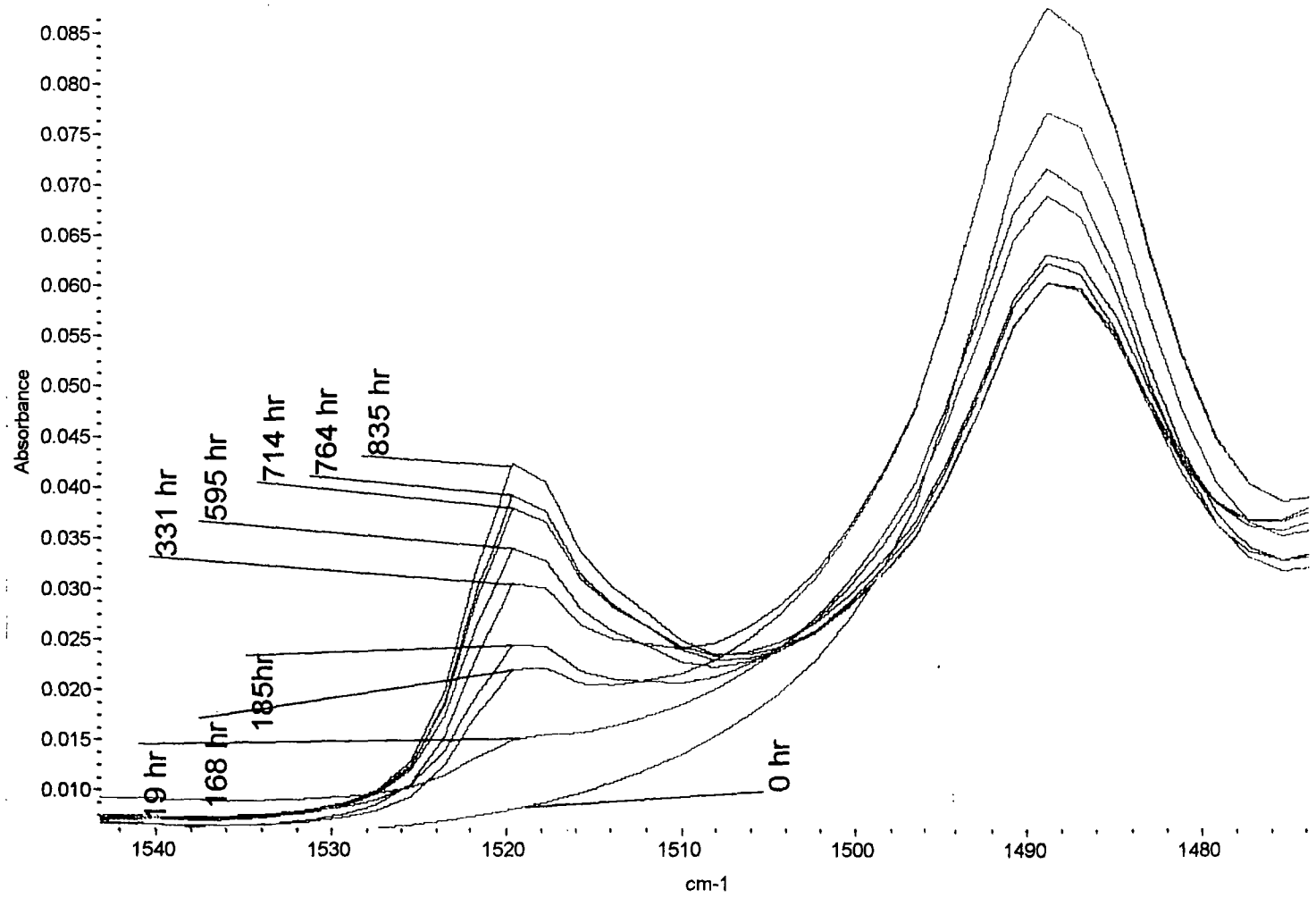
Method QC: Duplicate GPC Analysis Trends



View Comparison: FTIR Data



Analysis Details: FTIR Spectra From Aging Study



Material Fingerprinting Successes/Improvements (cont'd)

- **HC polymer,** carboxy terminated polybutadiene (CTPB)
  - **This liquid polymer is used in the liner that bonds the propellant to the case insulation.**
  - **Understanding the details of the polymer and the manufacturing process enabled analysts to identify a noxious byproduct at increased levels that was making operators sick.**
    - The bad lot was taken out of production and a corrective action was developed to improve the vendor's manufacturing process.
    - A detection and quantification method with new limits for the byproduct is in place for acceptance of future lots.
  - **In-depth fingerprinting knowledge has also been invaluable for the development of the replacement after current vendor announced the closure of their HC polymer plant.**
    - Initial carboxy terminated polybutadiene (CTPB) received from a new vendor showed distinct differences from HC polymer in small acids and molecular weights.
    - Recommendations to improve reaction mixture ratios as well as process washing and drying have enabled new vendor to produce acceptable polymer, now being tested for use on RSRM.
    - Also developing acceptance testing and spec limits for both commercial and defense programs with this new material.

Material Fingerprinting Successes/Improvements (cont'd)

- BRULIN 1990 GD-T
  - ODC replacement for methyl chloroform vapor degreasing
  - Water-based solvent used with spray-in-air technology
  - Several issues developed with material during certification
    - Material received with insoluble material in drums
    - Material received with lower than expected pH
  - Vendor asked for site visit from Thiokol's chemist
    - Knowledge from fingerprinting provided information to stabilize product through small changes in use of de-ionized water, mixing steps, and cycles
    - Use of hydrated silicates
  - Recommendation for KOH add back to spray-in-air baths
    - Increased useable bath life from 8 to 90 days
  - Knowledge from fingerprinting effort provided suggestion for corrosion inhibitor rinse cycle (new inhibitor currently qualified)

Material Fingerprinting Successes/Improvements (cont'd)

- MAPO (Methyl Aziridinyl Phosphine Oxide)
  - Used as a curative for the liner between insulation and propellant
  - Recent Lot received with incomplete certification
  - Acceptance testing indicated material was out of specification for reactive imine, hydrolyzable chloride and total chloride
  - Additional tests were done per the fingerprinting SLP that supported the previous testing and included GPC data that began to suggest the nature of the problem
  - Further testing using more detailed techniques (HPLC/MS) developed through fingerprinting in R&D Labs identified the process by-product impurities and aided vendor in finding a resolution
  - Material returned to vendor for reprocessing

Material Fingerprinting Successes/Improvements (cont'd)

- TCA – Methyl Chloroform
  - Ozone Depleting Chemical (ODC) TCA has limited availability due to restrictions for defined essential use.
  - A large amount of stored TCA had exceeded its shelf life and deteriorated out of specification.
    - Distillation was proposed as a recovery technique, but there was uncertainty on its effects on the stabilization components.
    - Fingerprinting analyses were able to prove the distilled material acceptable to NASA.
  - Basic understanding has also identified problems with long-term storage of the TCA from a second source due to incompatibility between two components in its stabilizer package.
  - Currently working with vendor, design and manufacturing engineers to assess new methods for storage to ensure this critical solvent will be available until a replacement solvent can be qualified or, if necessary, for the life of the RSRM program.

Material Fingerprinting Successes/Improvements (cont'd)

- Corrosion inhibiting grease from new plant verified with FTIR
  - Vendor tried a new formulation but reverted to original catalyst after fingerprinting confirmed it gave most consistent result
- D-limonene containing solvents removed from use on uncured rubber after testing confirms degradation of cure system
- BHT identified as a minor additive to inhibit d-limonene degradation in solvents
- Detailed fingerprinting of rubber to metal adhesives has provided new insight into aging processes plus new ways to monitor aging
  - Aging studies indicate resin interaction as early step in degradation
  - Significant reduction in shelf life with certain environments
  - New methods provide early warning of potential problems

Direct Benefits of Fingerprinting

- Fundamental understanding of critical materials that often equals or exceeds vendor's knowledge
  - Provide baseline chemical profile of materials in use
  - Material changes can often be traced to their source
- Standardized approach including:
  - Material team for focus and relevance
  - Flexible test plan for method adaptation or development
  - Laboratory team for technical expertise
  - Final report and R&D procedures to document method development
  - SLP of key down-selected robust methods in standard format for routine use in Process Control Lab
- Material team technical ownership
  - Analytical chemist as material specialist
  - Improved communication between procurement, work centers, quality and labs

Additional Benefits of Fingerprinting

- Versatile database broadly available both for new lot comparison and problem solving
  - Available plant-wide and informative on many levels of detail
  - Trending of key parameters and QC data as well as detailed overlay
  - Lot-to-lot consistency monitored and changes flagged
  - Security functions provide protection for vendor proprietary information
- Improved vendor relationships through data and method sharing
  - New methods shared with vendors to enhance their capabilities
  - Vendors acknowledge our expertise and expand cooperation by timely reporting of planned changes
- Greater efficiency and confidence in requalification/ qualification of materials due to obsolescence or changes in vendor or production site

Continuing Challenges

- Down selection for Process Control Lab
  - Basic chemical characterization
  - Methods robust and simple enough for routine analysis
  - Key component information – what is likely to go wrong next
    - History of materials and vendors
    - Dependable crystal ball
- Implementation in Process Control Lab
  - Training at higher level of technical expertise
  - Greater demands on LIMS and data entry
  - Setting limits for new acceptance criteria
- Data utilization
  - Continuing education of vendors and engineers

Acknowledgements

- Vision of NASA/MSFC and Thiokol management to see the benefits of a formal Fingerprinting Program
- NASA funding through Marshall Space Flight Center
- Data sharing cooperation of material vendors
- Analytical efforts of Thiokol material specialists, scientists, and engineers